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POLYARAMIDES WITH REACTIVE PHENYLETHYNYL PENDANTS



R. C. Evers
G. J. Moore
Polymer Branch
Nonmetallic Materials Division

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Tonson Abraham
University of Dayton
Research Institute
Dayton, OH 45469

April 1988

Final Report for Period July 1983 to July 1986

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19. (Abstract continued)

Isothermal aging in air of the cured specimen at 316°C (600°F) led to a 25 percent weight loss after 200 hrs.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 23303Q307, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. I. J. Goldfarb as the Materials Laboratory Project Scientist. Co-authors were Dr. R. C. Evers and Mr. G. J. Moore, Materials Laboratory, (AFWAL/MLBP) and Dr. Tonson Abraham, University of Dayton Research Institute.

This report covers research conducted from July 1983 to July 1986. The authors wish to thank Miss Danielle Daniels for her contribution to the synthesis operations. The thermal behavior data were contributed by Mr. E. J. Soloski and Dr. I. J. Goldfarb. Mr. C. Benner carried out the high performance liquid chromatography studies.

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TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II RESULTS AND DISCUSSION	4
Monomer Synthesis	4
Polymer Synthesis	6
Polymer Properties	8
III EXPERIMENTAL	13
Monomer Synthesis	13
Polymer Synthesis	22
REFERENCES	25

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Infrared Spectra of Uncured and Partially Cured Polymer VI (KBr Pellet)	10
2	Isothermal Aging of Cured Polymer VI in Air at 316°C (600°F)	12

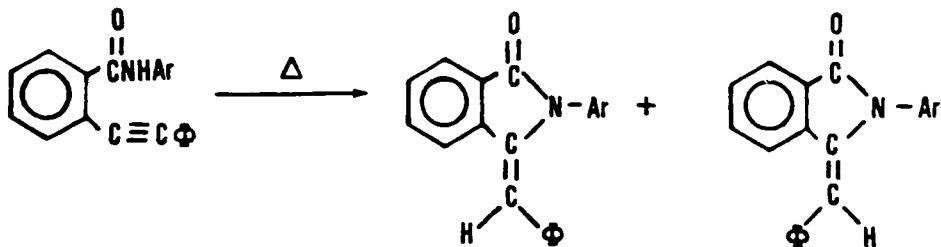
LIST OF TABLES

TABLE		PAGE
1	Viscosity Data of Aromatic Polyamides	7
2	Thermal Analytical Characterization of Aromatic Polyamides	8

SECTION I
INTRODUCTION

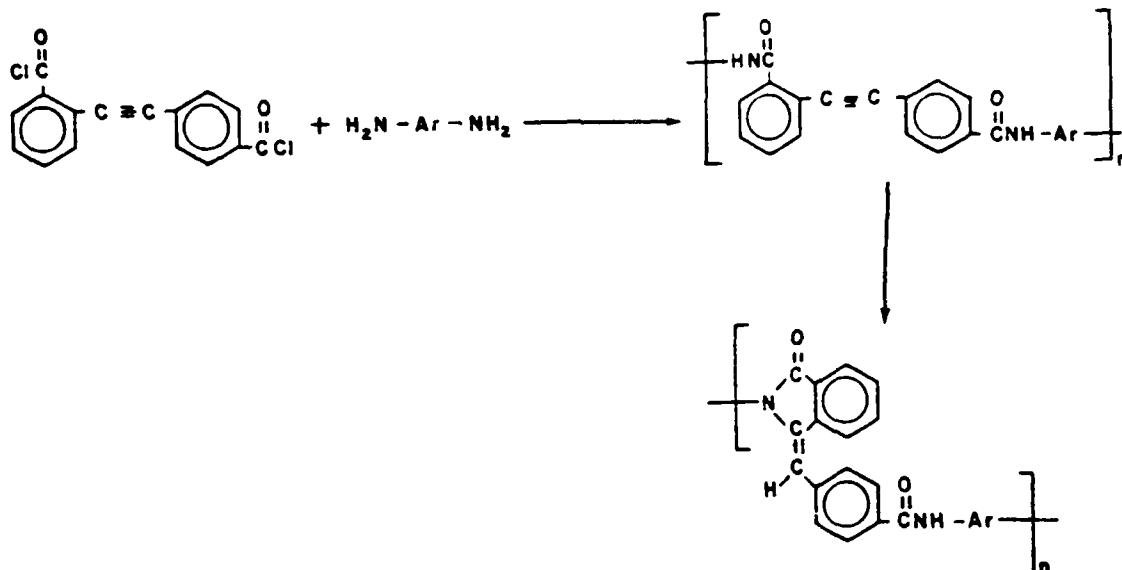
Earlier studies in this laboratory have been concerned with the curing of aromatic-heterocyclic matrix resins by intramolecular cycloaddition reactions (IMC). This type of cure has been demonstrated initially with phenylquinoxaline¹ and imide² polymers and involves starting with a linear, relatively mobile polymer chain which when heated reacts via an IMC reaction to form a thermooxidatively stable, aromatic system within the polymer backbone. The addition reaction transforms the polymer from a fairly flexible chain to a rigid backbone structure, thereby advancing the glass transition temperature (Tg) of the polymer and increasing its potential use temperature.

Previous IMC cures were based on the thermal conversion of 2,2-di(phenylethynyl)biphenyl to a highly fused anthracene structure.³ Another chemical structure which has been considered as a potential IMC cure site is N-phenyl-2-(phenylethynyl)-benzamide which has been shown to undergo thermal cycloaddition to a mixture of Z- and E-2,3-dihydro-2-phenyl-3-phenylmethylene-1H-isoindol-1-one⁴ or, more simply, benzalphthalimidine structures.

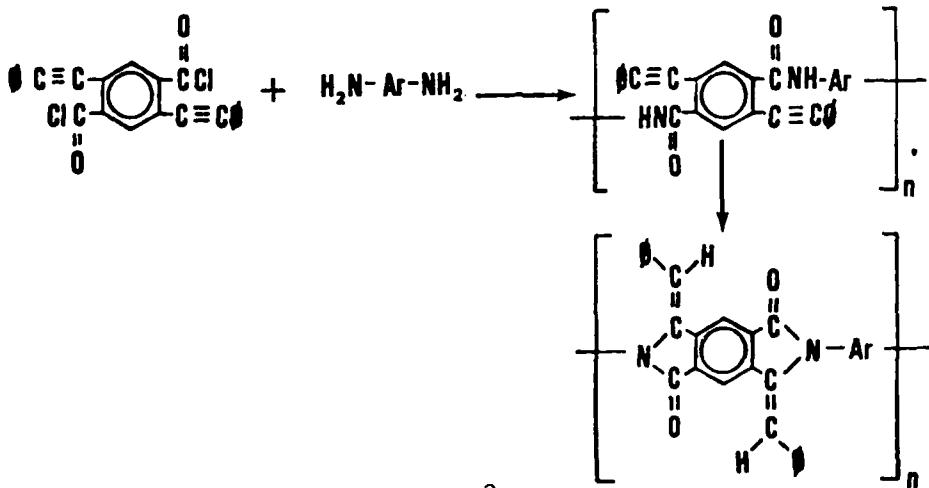


In order to incorporate this potential IMC site into a polymer structure, appropriate diacid chloride monomers were synthesized under the present effort and subjected to low-temperature polycondensation reactions with aromatic diamines to form thermally reactive aromatic polyamides (polyaramides). An initial feasibility study entailed polycondensation of the readily prepared tolane-2,4'-dicarbonyl chloride with aromatic

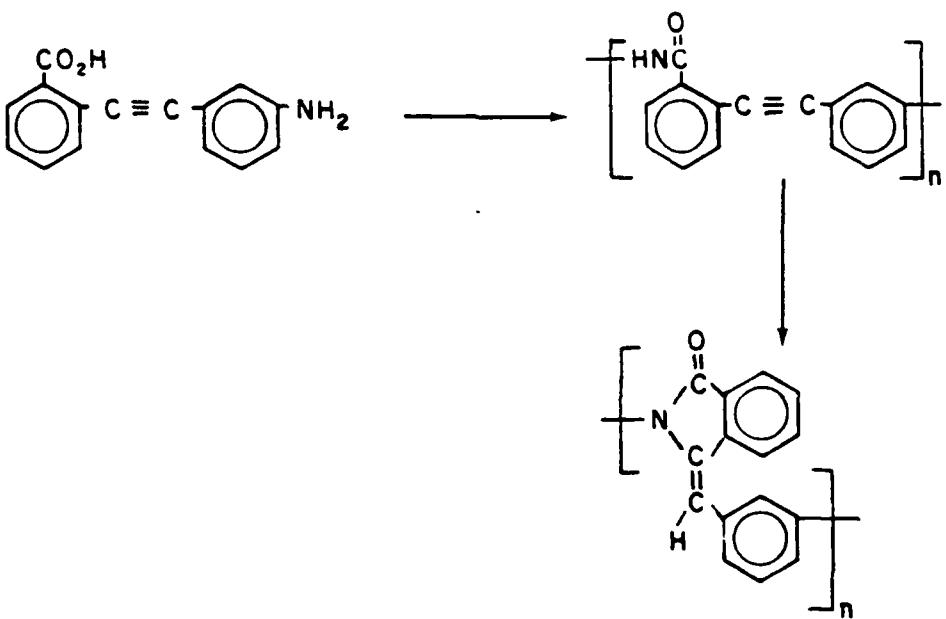
diamines and subsequent thermal treatment of the resultant polyaramides to effect cyclo-addition of the phenylethyne moiety with the ortho-amide group. The thermally treated product contained benzalphthalimidine groups in the polymer backbone as well as unreacted amide groups which were not in a position to undergo an IMC reaction.



Major emphasis was directed toward the synthesis of appropriately substituted isophthaloyl- and terephthaloyl-chloride monomers. Subsequent polycondensation with aromatic diamines afforded polyaramides which contained pendant phenylethyne substituents. In these polymers, all of the amide groups were potential participants in the IMC reaction to the benzalphthalimidine structure.



Additional effort was directed toward the preparation of 2-(3-aminophenylethynyl)benzoic acid and appropriate derivatives which, upon undergoing homopolymerizations, would yield thermally reactive polyaramides with a phenylethynyl moiety appropriately incorporated within the polymer backbone to permit intramolecular cyclization to the polybenzalphthalimidine structure.

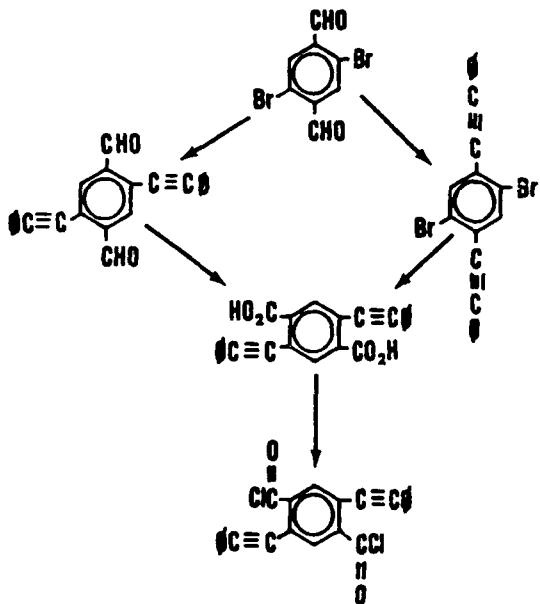


In this paper, the synthesis of these novel monomers and their subsequent polycondensation reactions are described. Properties of the resultant thermally reactive polyaramides are given as is polymer behavior upon thermal treatment to effect the IMC reactions.

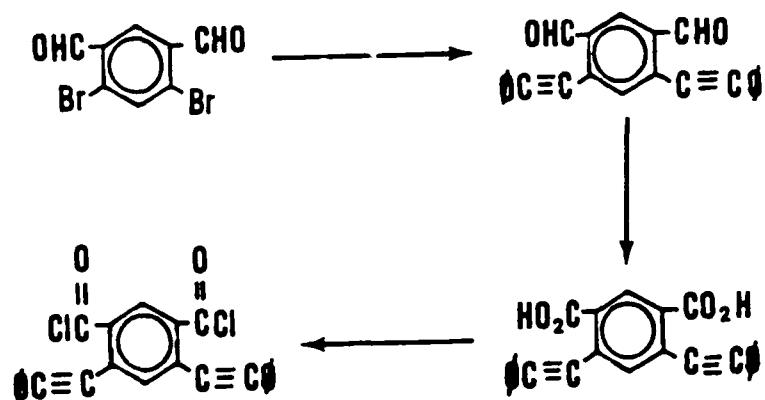
SECTION II
RESULTS AND DISCUSSION

Monomer Synthesis

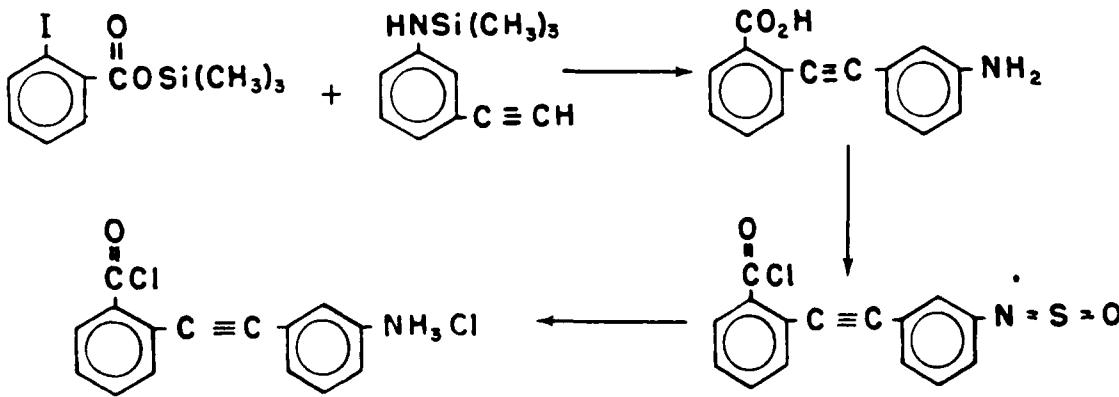
Initial synthesis attempts were directed toward the preparation of 2,5-bis(phenylethynyl)terephthaloyl chloride. Reaction of 2,5-dibromoterephthaldehyde with diphenyl(α -chlorobenzyl)-phosphonate in the presence of sodium hydride led to a 48 percent yield of 1,4-bis(phenylethynyl)-2,5-dibromobenzene. Treatment of this intermediate with n-butyl lithium and subsequent carbonation with dry ice gave a 53 percent yield of 2,5-bis(phenylethynyl)-terephthalic acid. Alternatively, this diacid could be prepared by the palladium-catalyzed reaction of 2,5-dibromoterephthaldehyde with phenylacetylene to give a 44 percent yield of 2,5-bis(phenylethynyl)terephthaldehyde. Selective oxidation in acetone with a mixture of chromium trioxide/sulfuric acid (Jones reagent⁵) resulted in a 98 percent yield of 2,5-bis(phenylethynyl)terephthalic acid. Conversion of this diacid to the requisite monomer, 2,5-bis(phenylethynyl)terephthaloyl chloride, was effected in 56 percent yield by treatment with thionyl chloride.



4,6-Bis(phenylethynyl)isophthaloyl chloride was subsequently synthesized by an analogous synthetic route. Reaction of 4,6-dibromoisophthaldehyde [prepared by the hydrolysis of 1,3-bis(dibromomethyl)-4,6-dibromobenzene] with phenylacetylene in a pyridine/triethylamine medium was catalyzed with palladium diacetate to give a 64 percent yield of 4,6-bis(phenylethynyl)-isophthaldehyde. Oxidation of this intermediate with Jones reagent⁵ led to an 85% yield of 4,6-bis(phenylethynyl)isophthalic acid which was then treated with thionyl chloride to give a 36 percent yield of the desired monomer.



2-(3-Aminophenylethynyl)benzoic acid was prepared in 35 percent yield by the palladium-catalyzed reaction of trimethylsilyl 2-iodobenzoate with 3-ethynyl-N-trimethylsilylaniline. This monomer, upon sequential reaction with thionyl chloride and with gaseous hydrogen chloride, was converted via the sulfinyl intermediate into the hydrochloride salt of 2-(3-aminophenylethynyl)benzoyl chloride.



In the synthesis of these monomers, precautions were taken to minimize exposure of the substituted carboxylic acids to heat in order to avoid the formation of lactone structures which result from cyclization of the carboxylic acid groups with the o-phenylethynyl groups.^{6,7} However, mass spectroscopy results for the diacid chloride monomers indicated that some cyclization did occur as reflected by the presence of minor impurities. In addition, high performance liquid chromatography (60 Å Porosil, CH₂Cl₂) demonstrated monomer purity of 97 percent with two minor impurities being present. Polymer molecular weight may have been limited due to the presence of these impurities.

Polymer Synthesis

Polycondensations of tolane-2,4'-dicarbonyl chloride, 2,5-bis(phenylethynyl)terephthaloyl chloride and 4,6-bis(phenylethynyl) isophthaloyl chloride with aromatic diamines [4,4'-oxydianiline or 4,4'-(m-phenylenedioxy)dianiline] were carried out in carefully dried N-methyl-2-pyrollidone (NMP) or N,N-dimethylacetamide (DMAC). The reactions were run at 0-5°C for several hours and then at room temperature overnight. The resultant polyaramides were isolated in almost quantitative yield by precipitation from methanol, purified by prolonged extraction with hot methanol, and dried at 100°C under high vacuum. Inherent viscosities of 0.20-0.51 dl/g were recorded (Table 1).

TABLE 1
VISCOSITY DATA OF AROMATIC POLYAMIDES

POLYMER	MONOMERS	η_{inh} - dl/g
I	Tolane-2,4'-dicarbonyl Chloride 4,4'-Oxydianiline	0.29 (a)
II	Tolane-2,4'-dicarbonyl Chloride 4,4'-(m-Phenylenedioxoy)dianiline	0.31 (a)
III	2,4-Bis(phenylethynyl)terephthaloyl Chloride 4,4'-Oxydianiline	0.30 (b)
IV	2,5-Bis(phenylethynyl)terephthaloyl Chloride 4,4'-(m-Phenylenedioxoy)dianiline	0.51 (b)
V	4,6-Bis(phenylethynyl)isophthaloyl Chloride 4,4'-Oxydianiline	0.20 (b)
VI	4,6-Bis(phenylethynyl)isophthaloyl Chloride 4,4'-(m-Phenylenedioxoy)dianiline	0.26 (b)

(a) = DMAC, 25°C, 0.2 g/dl

(b) = Methanesulfonic Acid, 25°C, 0.2 g/dl

Homopolymerization of 2-(3-aminophenylethynyl)benzoic acid in NMP under the influence of triphenyl phosphite at 80°C led to almost immediate precipitation of low molecular weight product which exhibited an inherent viscosity of 0.03 dl/g. Carrying out the reaction at 150°C yielded polymer which exhibited absorptions in the infrared spectrum indicative of IMC reaction. Polycondensation of the hydrochloride salt of 2-(3-aminophenylethynyl)-benzoyl chloride in NMP yielded a similar result. An inherent viscosity of 0.10 dl/g was recorded. An alternate approach to the desired polymer entailed the palladium-catalyzed polycondensation in NMP of 2-iodo-3'-ethynylanilide (prepared by condensation of 0-iodobenzoyl chloride and 3-ethynylaniline). Precipitation of product again occurred shortly after heating of the reaction mixture was initiated. The products obtained from these reactions are believed to be very low molecular polymer of

the expected structures as indicated by elemental analysis, infrared spectroscopy, and solution viscosity data. Polymer molecular weight may have been limited due to the low polymer solubility in the polymerization solvent and the resultant premature precipitation. Due to the low degree of polymerization, the polymers were not further characterized.

Polymer Properties

The aromatic polyamides listed in Table 1 were obtained as fluffy or fibrous, pale yellow solids which were readily soluble in methane sulfonic acid or DMAC/5 percent LiCl. They were somewhat less soluble in DMAC or NMP. Polymer structure was verified by elemental analysis and infrared spectroscopy. Infrared spectra exhibited absorptions at 3380, 3060, and 1670 cm^{-1} , indicative of aromatic amide groups, and at 2200 cm^{-1} , indicative of non-terminal alkyne. The thermal characteristics of the polymers were investigated by means of differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Results of the thermal characterization studies are summarized in Table 2.

TABLE 2
THERMAL ANALYTICAL CHARACTERIZATION OF AROMATIC POLYAMIDES

Polymer	Tg-°C	Onset T _{cure} -°C	Max T _{cure} -°C	Final Tg-°C
I	(a)	170	252	270
II	182	190	242	220
III	(a)	200	245	(b)
IV	189	222	250	(b)
V	(a)	185	250, 299	(b)
VI	174	195	255, 280	(b)

(a) No Tg noted. Possibly obscured by onset of cure.
(b) No Tg observed after scanning of 450°C.

All polymer samples exhibited exotherms attributable to the IMC reaction with onset occurring in the 170-225°C range. Only those polymers (II, IV and VI) derived from the higher molecular weight diamine, 4,4'-(*m*-phenylenedioxy)dianiline, exhibited an initial Tg. In the case of the less flexible polymers (I, III and V) derived from 4,4-oxydianiline, it is believed that any baseline shift attributable to the initial polymer Tg was hidden by the exotherm attributable to the IMC reaction. DSC and TMA data on the polyamides indicated that after heating to 450°C under nitrogen in the instrument, only polymers I and II showed an observable Tg upon reheating. These polymers, derived from tolane-2,4'-dicarbonyl chloride, contained only a single IMC site per repeat unit and would not be expected to exhibit Tg increases as substantial as polymers III-VI which contained two IMC sites per repeat unit. The latter polymers exhibited no indication of softening upon reheating. Subjecting a pressed pellet of polymer VI to similar thermal treatment produced an insoluble, very dark, brittle material which was characteristic of extensively cross-linked material. In addition to possible interchain reactions of the pendant phenylethynyl groups⁸, interchain reactions involving the exocyclic double bonds of the benzalphthalimidine structures may have taken place. Crosslinking of polyphthalimidines at elevated temperatures has been previously reported⁹. Thermal treatment under nitrogen of polymer VI as a pressed pellet for 16 hours at 250°C yielded a light brown specimen which was almost completely soluble in methanesulfonic acid. DSC and TMA study of the cured material disclosed a Tg of 275°C as well as softening and a residual exotherm in the 350-400°C region, possibly indicative of incomplete cyclization. This was borne out by the infrared spectrum of the cured sample which exhibited an absorption at 1670 cm⁻¹, indicative of residual aromatic amide carbonyl, as well as an absorption at 1720 cm⁻¹, attributable to the carbonyl group of the cyclized phthalimidine structure⁹. The change in polymer infrared spectrum is shown in Figure 1. The sample, upon heating to 450°C, exhibited an increase in Tg from 275°C to 308°C, indicative of more complete cyclization or crosslinking as well as possible concurrent degradation.

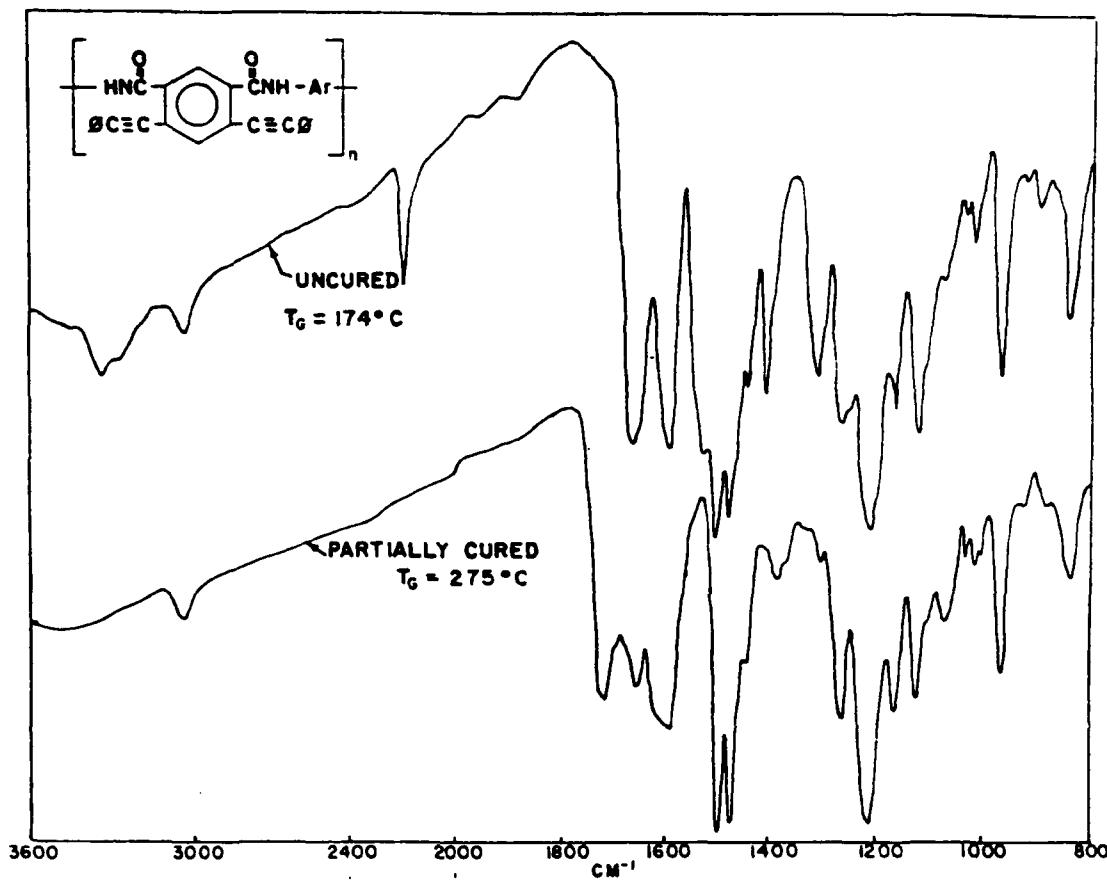


Figure 1. Infrared Spectra of Uncured and Partially Cured Polymer VI (KBr Pellet)

The thermooxidative stabilities of the aromatic polyamides were evaluated by thermogravimetric - mass spectral analysis and isothermal aging. Onset of weight loss under thermogravimetric analysis in an air atmosphere of cured as well as uncured samples occurred in the 395-410°C range with essentially complete weight loss having occurred by 700°C. These values compare favorably with published thermogravimetric analysis data for other aromatic polyphthalimidine structures.⁹ Mass spectral analysis of decomposition products obtained during thermogravimetric analysis under high vacuum indicated only the release of absorbed water below 300°C. No volatile products which would arise from degradation and/or condensation reactions inconsistent with the IMC reaction route were observed below this temperature. Isothermal aging in air at 316°C (600°F) of the cured sample described in the previous paragraph led to a weight loss of 25 percent after 200 hours. A representative isothermal aging curve is shown in Figure 2.

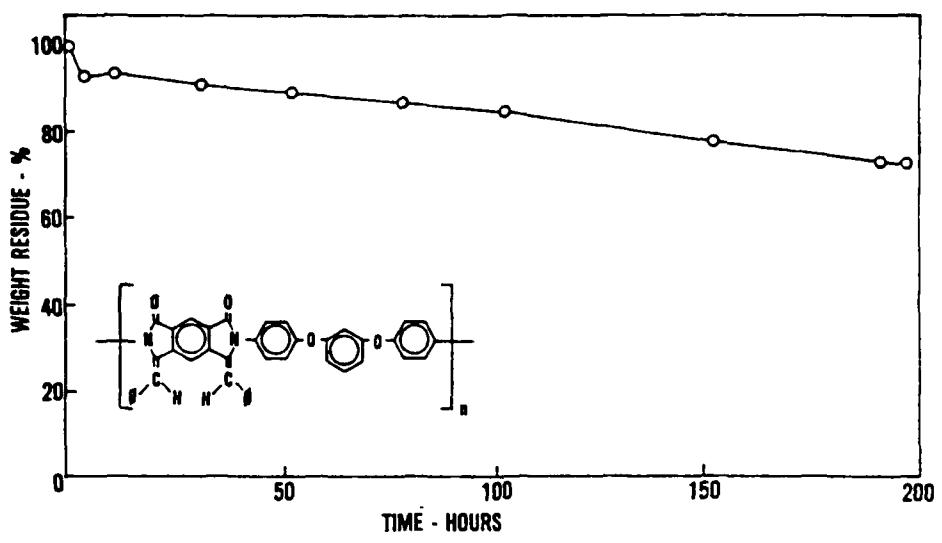


Figure 2. Isothermal Aging of Cured Polymer VI in Air at 316°C (600°F)

SECTION III
EXPERIMENTAL

Monomer Synthesis

The requisite monomers were either obtained from commercial sources and purified as necessary or synthesized according to the procedures described below.

Tolane-2,4'-dicarbonyl Chloride

2,4'-Tolanedicarboxylic acid⁷ (2.40 g, 0.009 moles) was stirred at room temperature for 48 hours in 35 ml of thionyl chloride (redistilled from boiled linseed oil). This suspension was then refluxed for eight hours to give a clear, light red solution. The excess thionyl chloride was then stripped off to give a grey solid, mp 79-85°C. Recrystallization from hexane (charcoal) (300 ml reduced to 100 ml) afforded 1.38 g (51 percent yield) of tolane-2,4'-dicarbonyl chloride as a waxy, off-white solid which after drying at 58°C/0.10 mm Hg exhibited mp 184.5-185.5°C.

Anal. Calc'd for C₆H₈Cl₂O₂: C, 63.39; H, 2.66; Cl, 23.39; MW, 266. Found: C, 63.42; H, 2.12; Cl, 23.21; MW, 266 (mass spectrum).

4,6-Bis(phenylethyanyl)isophthaloyl Chloride

Bromine (395.5 g, 2.472 mole, 127.5ml) (dried over concentrated sulphuric acid) was added dropwise to stirred 4,6-dibromo-1,3-xylene¹⁰ (150 g, 0.568 mole) in an ultraviolet irradiation apparatus. Approximately 90 ml of bromine was added over 2.5 hours with the temperature being maintained at 120-130°C. An additional 20 ml was added over two hours at 130-150°C and the final 17 ml was added over two hours at 150-160°C. After the bromine was completely taken up, the yellow reaction mixture was distilled in portions to give 1,3-bis(dibromomethyl)-4,6-dibromobenzene as a white solid, bp 178-182°C/0.02 mm Hg. Recrystallization from absolute ethanol yielded a total of 259 g (79 percent yield) of white crystals, mp 115.0-118.0°C.

Anal. Calc'd for $C_8H_4Br_6$: C, 16.58; H, 0.69; MW, 580.
Found: C, 16.49; H, 0.67; MW, 580 (mass spectrum).

An aqueous solution of silver nitrate (71.0 g, 0.418 mole) in 544 ml of water was added dropwise over three hours to a stirred solution of 1,3-bis(dibromomethyl)-4,6-dibromobenzene (40.0 g, 0.069 mole) in 300 ml of cellosolve at 80-85°. The green reaction mixture was stirred at temperature for an additional .5 hours and filtered while hot. The collected precipitate was washed thoroughly with water and suction dried on the frit. Water added to the filtrate produced a white product that was recrystallized from cyclohexane to yield 6.1 g of white crystals. The dried green precipitate was extracted with hot benzene and the resulting material recrystallized from cyclohexane to yield 7.1 g of white crystals. Combined yield of 4,6-dibromoisophthalaldehyde was 13.6 g (66 percent yield), mp 188.0-191.0°C.

Anal. Calc'd for $C_8H_4Br_2O_2$: C, 32.91; H, 1.38; MW, 292.
Found: C, 32.83; H, 1.46; MW, 292 (mass spectrum).

4,6-Dibromoisophthalaldehyde (16.4 g, 0.056 mole) was dissolved in a solution of triethylamine (280 ml) and pyridine (315 ml) under a nitrogen atmosphere. To the stirred solution were added palladium acetate (0.28 g, 0.0013 mole) and triphenyl phosphine (0.70 g, 0.0027 mole). Phenylacetylene (14.3 g, 0.140 mole) was added dropwise over the course of an hour to the red reaction mixture at 45-50°C. The reaction was continued an additional 3.5 hours. The reaction mixture was then cooled and poured into a sulfuric acid-ice mixture. The resultant yellow precipitate was collected by filtration, thoroughly washed with water, and suction dried on the frit. Recrystallization of the material from heptane yielded 12.0 g (64 percent yield of 4,6-bis(phenylethylynal)isophthalaldehyde, mp 170.0-172.0°C.

Anal. Calc'd for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22; MW, 334.
Found: C, 85.56; H, 4.40; MW, 334 (mass spectrum).

4,6-Bis(phenylethylynal)isophthalaldehyde (7.8 g, 0.023 mole) was dissolved in acetone (distilled from solid potassium

permanganate) and the solution was chilled to 0°C. A chromium trioxide-sulfuric acid solution was prepared by slurring 26.7 g of chromium trioxide in 23 ml of concentrated sulfuric acid and 40 ml of distilled water. This solution was diluted in the cold with distilled water to 110 ml. A portion of this solution (16.9 ml) was added dropwise over 1.5 hours to the stirred yellow acetone solution. During this period the color of the reaction mixture changed from yellow to brown and finally to green. After an additional 20 hours of reaction, the mixture was warmed to room temperature and poured into a vessel containing ice and water. The yellow precipitate was collected by filtration and washed thoroughly with water. Suction drying on the frit yielded 7.3 g (85 percent yield) of light yellow 4,6-bis(phenylethynyl)-isophthalic acid.

Anal. Calc'd for $C_{24}H_{14}O_4$: C, 78.68; H, 3.85; MW, 366.
Found: C, 78.88; H, 3.95; MW, 366 (mass spectrum).

4,6-Bis(phenylethynyl)isophthalic acid (4.0 g, 0.0109 mole) was slurried in 170 ml of thionyl chloride (freshly distilled from boiled linseed oil) for 30 minutes. A few drops of N,N-dimethylformamide was added to the reaction mixture to effect solution. The reaction mixture was stirred between 35-40°C for 16 hours. Removal of the excess thionyl chloride under reduced pressure yielded an orange-yellow solid. Recrystallization from hexane gave 16 g (36.4 percent yield) of 4,6-bis(phenylethynyl)-isophthaloyl chloride as light yellow crystals, mp 157.0-160.0°C.

Anal. Calc'd for $C_{24}H_{12}Cl_2O_2$: C, 71.48; H, 3.00; MW, 402.
Found: C, 70.95; H, 3.32; MW, 402 (mass spectrum).

2,5-Bis(phenylethynyl)terephthaloyl chloride (Method 1)

2,5-Dibromo-1,4-xylene¹¹ (43.0 g, 0.163 mole) was dissolved in 550 ml of glacial acetic acid and 550 ml of acetic anhydride. To the vigorously stirred solution at 0-5°C was cautiously added 90 ml of concentrated sulfuric acid. With the temperature being maintained at -5°C, chromium trioxide (93.0 g, 0.930 mole) was gradually added over a period of 1.5 hours, care being taken to

keep the reaction temperature below 5°C. The red reaction mixture gradually became very viscous and took on a deep green coloration. After being stirred for four more hours, it was then brought to room temperature and poured with stirring into five liters of cold water. The white precipitate was isolated by filtration and washed on the frit with water until no green color appeared in the washings. The white solid was stirred in two liters of two percent sodium carbonate solution for one hour, isolated by filtration, and washed well on the frit with water. Air drying overnight afforded 45.5 g (56 percent yield) of unpurified 2,5-dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetraacetoxy-1,4-xylene, mp 200-210°C. Recrystallization of an analytical sample from isopropanol gave mp 219.0-221.0°C.

Anal. Calc'd for $C_{16}H_{16}O_8Br_2$: C, 38.73; H, 3.25; Br, 32.22. Found: C, 39.01; H, 3.08; Br, 32.11.

Unpurified 2,5-dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetraacetoxy-1,4-xylene (60.5 g, 0.122 mole) was dissolved with stirring in three liters of hot ethanol. Then 450 ml of water was added followed by 75 ml of concentrated sulfuric acid which was added very slowly. After being allowed to reflux for an hour, the reaction mixture was diluted with 900 ml of hot water. Cooling overnight at -10°C resulted in the crystallization of 30.9g (87 percent yield) of 2,5-dibromoterephthalaldehyde, mp 184.0-189.0°C. (lit 189.0-190.5°C)¹¹ which was isolated by filtration.

Anal. Calc'd for $C_8H_4O_2Br_2$: C, 32.91; H, 1.38; Br, 54.75; MW, 292. Found: C, 32.68; H, 0.90; Br, 54.60; MW, 292 (mass spectrum).

A solution of diphenyl(α -chlorobenzyl)phosphonate¹² (28.70 g, 0.080 mole) in 150 ml of dry dimethylsulfoxide was cooled to 0-5°C. Sodium hydride (3.84 g, 0.160 mole) (as a 50 percent suspension in mineral oil) was added to the rapidly stirred solution. The resultant foaming subsided after 30 minutes to give a deep purple solution. With the temperature being maintained at 0-5°C, 2,5-dibromoterephthalaldehyde (11.64 g, 0.04 mole) slurried in 50 ml of dry dimethylsulfoxide and was added over a five minute period. Considerable foaming

took place during the addition. After being allowed to continue at room temperature overnight, the reaction mixture was added to 250 ml of ice water. The resultant beige precipitate was isolated by filtration and washed on the frit with water. Drying at 60°C/1.0 mm Hg for two hours yielded 16.63 g of beige product, mp 130-235°C. The crude product was extracted with 400 ml of heptane for two hours in an extraction apparatus. The heptane solution upon cooling gave 8.45 g (48 percent yield) of 1,4-bis(phenylethynyl)-2,5-dibromobenzene as light yellow crystals, mp 155.0-158.0°C. An additional 3.5 g of slightly lower melting material was recovered from the mother liquor.

Anal. Calc'd for $C_{22}H_{14}Br_2$: C, 60.58; H, 2.77; Br, 36.65; MW, 436. Found: C, 60.85, H, 2.52; Br, 36.41; MW, 436 (mass spectrum).

n-Butyl lithium (2.11 g, 0.033 mole) (14.25 ml of a 2.23M solution in hexane) was added over five minutes to a vigorously stirred solution of 1,4-bis(phenylethynyl)-2,5-dibromobenzene (6.54 g, 0.015 mole) in 500 ml of ether at 0°C. The initial yellow slurry took on a brown color for several minutes before a dull yellow precipitate was formed. After being allowed to stir for three hours at 0°C under a nitrogen blanket, the reaction mixture was added to a slurry of dry ice in 300 ml of ether. This slurry was stirred for five hours and the excess dry ice was then allowed to evaporate. The ether solution was then extracted with 500 ml of a very dilute aqueous potassium hydroxide solution which was in turn extracted with 50 ml of ether. The cooled aqueous layer was acidified with dilute sulfuric acid to give a yellow precipitate which was isolated by filtration. Drying for three hours at 60°C/1.0 mm Hg yielded 5.10 g of crude product, mp > 360°C with prior shriveling at 190-200°C. Recrystallization from isopropanol (charcoal) (500 ml reduced to 150 ml) afforded 2.90 g (53 percent yield) of 2,5-bis(phenylethynyl)terephthalic acid as a powdery yellow solid, mp > 360°C with shrinking at 270-275°C.

Anal. Calc'd. for $C_{24}H_{14}O_4$: C, 78.68; H, 3.85; MW, 366. Found: C, 78.72; H, 3.65; MW, 366 (mass spectrum).

A mixture of 2,5-bis(phenylethynyl)terephthalic acid (2.20 g, 0.006 mole) suspended in 40 ml of thionyl chloride (distilled from boiled linseed oil) was stirred overnight at reflux to give a deep yellow solution. The excess thionyl chloride was stripped off to give a deep yellow solid which was recrystallized from 150 ml of heptane (charcoal). 2,5-Bis(phenylethynyl)terephthaloyl chloride (1.35 g, 56 percent yield) was obtained as deep yellow crystals, mp 179.0-181.0°C with prior shrinking at 176°C.

Anal. Calc'd. for $C_{24}H_{12}O_2Cl_2$: C, 71.48; H, 3.00; MW, 403. Found: C, 71.30; H, 2.91; MW, 403 (mass spectrum).

2,5-Bis(phenylethynyl)terephthaloyl Chloride (Method 2)

2,5-Dibromoterephthalaldehyde¹¹ (29.2 g, 0.100 mole) and phenylacetylene (25.5 g, 0.250 mole) were dissolved at 80°C under nitrogen in a mixture of freshly distilled triethylamine (200 ml) and pyridine (200 ml). Palladium acetate (0.54 g, 0.0024 mole) and triphenylphosphine (1.26 g, 0.0048 mole) were added to the vigorously stirred red solution. The resultant exotherm did not subside for fifteen minutes and a voluminous white precipitate was formed. After an additional one hour at reflux, the red slurry was added with vigorous stirring to a sulfuric acid-ice mixture. The slightly gummy brown precipitate was washed several times with water in a blender and isolated by filtration. It was dried overnight over phosphorus pentoxide at 80°C/1.0 mm Hg to yield 39.5 g of light brown solid, mp 145-162°C. The crude product was recrystallized from toluene (charcoal) (1400 ml reduced to 600 ml) to give 17.5 g of golden crystals, mp 174-179°C. Subsequent recrystallization from ethyl acetate gave 14.6 g (44 percent yield) of 2,5-bis(phenylethynyl)-terephthalaldehyde, mp 179.0-181.0°C.

Anal. Calc'd. for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22; MW, 334. Found: C, 86.42; H, 4.42; MW 334 (mass spectrum).

2,5-Bis(phenylethynyl)terephthalaldehyde (5.01 g, 0.015 mole) was stirred under nitrogen in 300 ml of redistilled acetone at 0°C. Then a chromium trioxide/sulfuric acid solution

(11.25 ml containing 3.0 g, 0.030 mole of chromium trioxide) was pipetted into the yellow slurry which was then stirred for four hours at 0°C. An additional 1.88 ml of chromium trioxide/sulfuric acid solution was then added and the reaction was allowed to proceed to 0°C for an additional two hours. The resultant slurry was poured into 600 ml of ice water and the yellow precipitate was isolated by filtration. After being washed well on the frit with water, the yellow solid was allowed to dry on the frit. Drying for one hour at 50°C/1.0 mm Hg over phosphorus pentoxide afforded 5.40 g (98 percent yield) of 2,5-bis(phenylethynyl)terephthalic acid, mp>360°C with slight shrinking at 260-270°C.

2,5-Bis(phenylethynyl)terephthalic acid (5.40 g 0.015 mole) was stirred at room temperature in 320 ml of thionyl chloride (distilled from boiled linseed oil). Several drops of N,N-dimethylformamide were added to the yellow slurry which was stirred overnight at room temperature. The small amount of insolubles which remained then went into solution after ten minutes at reflux. The excess thionyl chloride was stripped off at reflux to give an orange solid which was recrystallized from heptane (charcoal) to give 2.4 g (40 percent yield) of 2,5-bis(phenylethynyl)terephthaloyl chloride, mp 176.5-180.0°C.

2-(3-Aminophenylethynyl)benzoic Acid

Trimethylsilyl 2-iodobenzoate (prepared from reaction of 2-iodobenzoic acid and N,N-diethyltrimethylsilylamine) (19.8 g, 0.062 mole) and 3-ethynyl-N-trimethylsilylaniline (prepared from reaction of 3-ethynylaniline and N,N-diethyltrimethylsilylamine) (11.7 g, 0.062 mole) were stirred for 5 min in 100 ml of anhydrous triethylamine (distilled from calcium hydride) while nitrogen was being bubbled through the solution. Bistriphenylphosphinepalladium(II) chloride (0.9 g), cuprous iodide (0.25 g), and triphenylphosphine (1.4 g) were then added, and the reaction mixture was heated overnight to 80-90°C under nitrogen. The cooled solution was then extracted with water, cooled (ice), and acidified with concentrated hydrochloric acid in order to yield the hydrochloride salt of the title compound as a white

precipitate. The precipitate redissolved on further addition of concentrated hydrochloric acid. Sodium hydroxide pellets were then added to this solution to adjust the pH to 3. The off-white precipitate (10.5 g) that formed was isolated by filtration and recrystallized three times from methanol/water. Thus 5.2 g (35 percent yield) of product was obtained, mp 126.0-127.0°C. The recrystallization solution was heated to just below its boiling point. Overheating the solution led to decreased yields and an inferior product.

Anal. Calc'd. for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.91; MW 237. Found: C, 75.38; H, 4.78; N, 5.72; MW, 237 (mass spectrum).

2-(3-Aminophenylethynyl)benzoyl Chloride Hydrochloride

2-(3-Aminophenylethynyl)benzoic acid (0.90 g, 3.8 mmole) was stirred under nitrogen at reflux with 20 ml of thionyl chloride (distilled from boiled linseed oil). A golden solution formed almost immediately. After four hours reaction time, the excess thionyl chloride was stripped off and the residue was recrystallized from heptane to give 0.72 g (61 percent yield) of 2-(3-sulfinylaminophenylethynyl)benzoyl chloride as yellow crystals, mp 101.0-102.5°C.

Anal. Calc'd. for $C_{15}H_8NO_2SCl$: C, 59.69, H, 2.68; N, 4.64; S, 10.63; Cl, 11.76; MW, 302. Found: C, 59.74; H, 2.75; N, 4.97; S, 10.26; Cl, 11.96; MW, 302 (mass spectrum).

2-(3-Sulfinylamino phenylethynyl)benzoyl chloride (0.70 g, 2.3 mmole) was dissolved in 50 ml of anhydrous ether. Anhydrous hydrogen chloride was bubbled through the cooled, stirred solution to precipitate the hydrochloride salt as a white solid which was isolated by filtration under nitrogen. Drying at 58°C/0.10 mm Hg gave 0.45 g (67 percent yield) of 2-(3-amino-phenylethynyl)benzoyl chloride hydrochloride.

Anal. Calc'd. for $C_{15}H_{11}NOCl_2$: C, 61.66; H, 3.80; N, 4.79; Cl, 24.28. Found: C, 61.15; H, 3.93; N, 4.86; Cl, 24.10.

2-Iodo-3'-ethynylbenzanilide

Freshly distilled 3-ethynylaniline (1.55 g, 0.13 mole) in anhydrous ether (10 ml) was added dropwise under nitrogen to a cooled (ice-bath) solution of freshly distilled o-iodobenzoyl chloride (3.5 g, 0.03 mole) in 200 ml of anhydrous ether containing 5.0 ml of anhydrous triethylamine (distilled from calcium hydride). After stirring for one hour at room temperature, the salts were filtered off, and the ether filtrate was washed with water, dried over magnesium sulfate, and evaporated to a crude solid which was recrystallized from methylene chloride/hexane to give 3.5 g of product (77 percent yield), mp 140.0-140.5°C. The melting point rose to 140.5-141.5°C on further recrystallization.

Anal. Calc'd. for $C_{15}H_{10}INO$: C, 51.89; H, 2.90; N, 4.03; I, 36.55; MW, 347. Found: C, 51.91; H, 2.92; N, 4.15; I, 36.43; MW, 347.

Polymer Synthesis

Typical experimental procedures for the synthesis of phenylethynyl-substituted aromatic polyamides are given below.

Polycondensation of Tolane-2,4'-dicarbonyl chloride with 4,4'-(m-Phenylenedioxy)dianiline

4,4'-(m-Phenylenedioxy)dianiline¹³ (0.6724 g, 0.0023 mole) was dissolved in 5 ml of NMP (distilled from calcium hydride) and the resultant water-white solution was cooled to 0°C. Tolane-2,4'-dicarbonyl chloride (0.6972 g, 0.0023 mole) followed by 8 ml of N-methyl-2-pyrollidone was added to the vigorously stirred solution. The resultant pale green solution was stirred at 0°C for an hour and at room temperature for 36 hours. The polymer was precipitated from methanol and was washed with methanol in a continuous extraction apparatus for 36 hours. Drying at 58°C/0.10 mm Hg for 16 hours gave 1.0 g (83 percent yield) of cream colored polymer: $\eta_{inh} = 0.31 \text{ dl/g}$ (N,N-dimethylacetamide, 25°C, 0.2 g/dl).

Anal. Calc'd. for C₃₄H₂₂N₂O₄: C, 78.15; H, 4.24; N, 5.36.
Found: C, 78.07, H, 4.23; N, 5.40.

Polycondensation of 2,5-Bis(phenylethynyl)terephthaloyl Chloride with 4,4'-(m-Phenylenedioxy)dianiline

4,4'-(m-Phenylenedioxy)dianiline¹³ (0.5847 g, 0.0020 mole) was dissolved in 10 ml of DMAC (distilled from calcium hydride). The resultant water-white solution was cooled under nitrogen to 0°C. 2,5-Bis(phenylethynyl)terephthaloyl chloride (0.8065 g, 0.0020 mole) was added as a solid to the vigorously stirred solution over a five minute period. Three ml of N,N-dimethyl-acetamide were used to wash residual diacid chloride into the reaction flask. The resultant yellow slurry gradually became a clear pale green solution over the course of thirty minutes. After being stirred for three hours at 0°C and sixteen hours at room temperature, the slightly viscous solution was a pale yellow color. The polymer was isolated by precipitation from methanol and washed several times with methanol in a blender. Drying at 58°C/0.10 mm Hg for eight hours and at 100°C/0.1 mm Hg for four

hours gave 1.2 g (96 percent yield) of fluffy yellow polymer:
 $\eta_{inh} = 0.51 \text{ dl/g}$ (MeSO_3H , 25°C , 0.2g/dl).

Anal. Calc'd. for $\text{C}_{42}\text{H}_{38}\text{N}_2\text{O}_4$: C, 81.01; H, 4.21; N, 4.50.
Found; C, 81.07, H, 4.24; N, 4.38.

Polycondensation of 2-(3-Aminophenylethynyl)benzoyl
Chloride Hydrochloride

The hydrochloride salt of 2-(3-aminophenylethynyl)benzoyl chloride (0.40 g, 0.0014 mole) was suspended with stirring in 20 ml of cold (0°C) NMP (distilled from calcium hydride). Dried lithium carbonate (0.10 g, 0.0014 mole) was added to the suspension. Upon gradual warming to room temperature, the monomer appeared to dissolve. Almost concurrently, a colloidal suspension formed which was stirred at room temperature for several hours. The product was isolated by precipitation from methanol and subsequent filtration. It was extracted with methanol in a Soxlett extraction apparatus for 36 hours and dried at $100^\circ\text{C}/0.5 \text{ mm Hg}$ for 6 hours to give 0.26 g (86 percent yield) of cream-colored product: $\eta_{inh} = 0.10 \text{ dl/g}$ (MeSO_3H , 25°C , 0.2g/dl).

Anal. Calc'd. for $\text{C}_{15}\text{H}_9\text{NO}$: C, 82.17; H, 4.14; N 6.39.
Found: C, 81.80; H, 4.22; N, 6.16.

Polycondensation of 2-(3-Aminophenylethynyl)benzoic Acid

The monomer (0.6 g, 0.0025 mole) was slurried under nitrogen in 8 ml of dry NMP which contained 0.45 g of dry lithium chloride. To the cold stirred suspension was added 0.66 ml of triphenyl phosphite in 1.2 ml of pyridine. The reaction mixture became clear on warming as the lithium chloride dissolved. After one hour at 80°C , a colloidal suspension appeared. After an additional seven hours of reaction time, the product was precipitated from methanol and isolated by filtration. It was extracted with methanol in a Soxlett extraction apparatus for 36 hours. Drying at $100^\circ\text{C}/0.10 \text{ mm Hg}$ for eight hours yielded 0.35 g (64 percent yield) of cream colored polymer: $\eta_{inh} = 0.03 \text{ dl/g}$ (MeSO_3H , 25°C . $0/2 \text{ g/dl}$).

Polycondensation of 2-Iodo-3'-ethynylbenzanilide

The monomer (0.5 g, 0.0014 mole) was dissolved in a solution of 5 ml of dry NMP and 1 ml of dry triethylamine. To the water-white solution was added triphenyl phosphine (0.04 g), cuprous iodide (0.03 g), and bis(triphenylphosphine)palladium(II) chloride (0.15 g). After being stirred overnight under nitrogen at 80°C, the reaction mixture was transformed into a colloidal suspension which was poured into methanol to precipitate the product. The pale yellow product was washed repeatedly with methanol, and dried at 58°C/0.10 mm Hg overnight. Only 0.15 g (50 percent yield) of polymer was obtained; η_{inh} (MeSO_3H , 25°C, 0.2 g/dl) was negligible.

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